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Atmospheric Transport of Toxaphene to Lake Michigan

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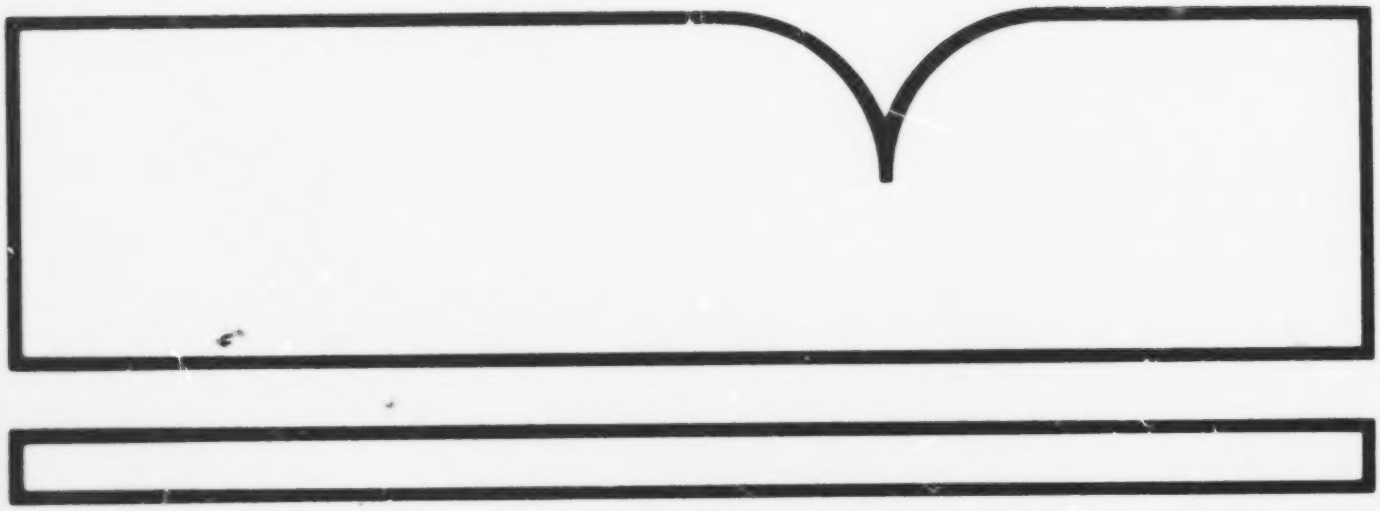

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16. ABSTRACT

■ Atmospheric levels of toxaphene were monitored during the summer and fall of 1981 at four locations: Greenville, MS; St. Louis, MO; Bridgman, MI; Beaver Island, MI. Each collection was conducted by continuously sampling air during the first 2 weeks of the months of August, September, October, and November. The collected toxaphene was analyzed on a capillary equipped electron capture gas chromatograph. The average concentrations over the entire sampling period for each site were 7.0 ng/m^3 in Greenville, 1.3 ng/m^3 in St. Louis, and 0.29 ng/m^3 for Lake Michigan (Bridgman and Beaver Island combined). The trend in relative levels of toxaphene was similar at each site. Levels were moderate in August, peaked for the September collections, returned to moderate levels in October, and declined to low levels for the November samples. Diagnostic modeling to describe possible air transport of toxaphene showed that at all receptor locations the air transport corridor for toxaphene was associated with southerly winds. The strength of this corridor increased from northern to southern measurement sites.

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Atmospheric Transport of Toxaphene to Lake Michigan

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■ Atmospheric levels of toxaphene were monitored during the summer and fall of 1981 at four locations: Greenville, MS; St. Louis, MO; Bridgman, MI; Beaver Island, MI. Each collection was conducted by continuously sampling air during the first 2 weeks of the months of August, September, October, and November. The collected toxaphene was analyzed on a capillary equipped electron capture gas chromatograph. The average concentrations over the entire sampling period for each site were 7.0 ng/m^3 in Greenville, 1.3 ng/m^3 in St. Louis, and 0.29 ng/m^3 for Lake Michigan (Bridgman and Beaver Island combined). The trend in relative levels of toxaphene was similar at each site. Levels were moderate in August, peaked for the September collections, returned to moderate levels in October, and declined to low levels for the November samples. Diagnostic modeling to describe possible air transport of toxaphene showed that at all receptor locations the air transport corridor for toxaphene was associated with southerly winds. The strength of this corridor increased from northern to southern measurement sites.

Introduction

Occurrence of toxaphene in the Great Lakes ecosystem is possibly one of the most perplexing pollution problems to have ever occurred in this region. Detectable levels of toxaphene were first evident in fish collected in 1974 from Lake Michigan and reported by the U.S. Fish and Wildlife Service (*1*). Subsequent to this, additional data have been reported that show toxaphene as a widespread contaminant of Great Lakes fish (*2*). However, the use of toxaphene is primarily concentrated in the southern states with few known applications of this pesticide in the Great Lakes region. The sources of toxaphene input to the Great Lakes have not yet been determined. Difficulty in analyzing environmental samples for toxaphene has prevented thorough examination of the occurrence and distribution of toxaphene in the environment.

Like PCB (polychlorinated biphenyls), toxaphene is not just one compound. In fact, it is a mixture of at least 180 separate chemical compounds (*3*). The complex chemical makeup of toxaphene is the primary reason that its environmental fate is so poorly understood. Conventional packed column separation with electron capture detection is not adequate to precisely characterize toxaphene. Fortunately, capillary chromatography techniques have allowed better resolution of the component peaks and have improved the confidence with which toxaphene is identified in samples. However, selective weathering of the original toxaphene peaks is believed to greatly alter the ratio of peaks from the parent material (*4*), as well as create new peaks that are derived from the parent toxaphene but cannot be used for matching and quantification in the usual sense. In a study of the global distribution of toxaphene, Zell and Ballschmiter (*4*) presented a technique using capillary separation and analysis of fish residues for chlorinated hydrocarbons which dealt with many of the analytical difficulties presented by toxaphene. In this method, fractionation of the extracts with Florisil chromatography was carried out to reduce interferences from PCBs. This type of approach has also been successfully applied by others. Ribick et al. (*5*) have analyzed fish tissues for toxaphene using silica gel fractionation and capillary chromatography while others have relied on silica or Florisil separation and packed column analyses (*6–8*). All of these techniques are based on chromatographic methods which rely on retention time matching as the basis for identification. However, these techniques do not provide absolute chemical confirmation. Exact chemical identification of environmental residues is further complicated by the fact that levels are usually low and many interference compounds are present. Furthermore, the components of toxaphene are difficult to measure by standard electron impact mass spectrometry due to their high fragmentation. Positive chemical ionization techniques with mass spectrometry show more promise, and recently some toxaphene components in fish from the Great Lakes have been verified by Ribick and co-workers (*5*).

The perplexing question about toxaphene's presence in the Great Lakes is "How is it getting there?" The choices are limited as uses of this insecticide in the Great Lakes area are few, with the preponderant uses occurring in the cotton and soybean growing areas of the southern United States (the Cotton Belt). Applications have shifted to include soybean farming, which extends up the Mississippi Valley beyond the usual limits for cotton farming; however, its use in 1984 was still predominantly in the southern portion of the U.S. About 86% of all cropland treated with toxaphene in 1981 was located in the south (C. Menzie, 1982, personal communication). Some use has been reported for the Great Plains States; however, for 1972 the total of 230 metric tons used by all the states from the

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region was only 1% of the Cotton Belt usage. In 1980, South Dakota used about 64 metric tons of toxaphene which would represent about 1% of estimated 1980 U.S. usage (*2*). No evidence for accidental spillage has been uncovered, and manufacturing is not located in any of the Great Lake states. One proposal contended that pulp bleaching may inadvertently produce toxaphene-like materials in its waste liquor. However, controlled laboratory tests under optimal conditions for chlorine substitutions of pulping waste liquors could not produce toxaphene-like compounds with greater than three chlorine atoms (presented by David Stalling, U.S. Fish and Wildlife Service, at EPA hearing for cancellation of toxaphene, July 1982); toxaphene is composed mainly of six to nine chlorine-containing compounds. To many scientists, the only logical choice left seems to be atmospheric transport. Direct observations of this, however, are limited.

There is a good deal of experimental evidence to suggest that chemicals like toxaphene, PCB, and DDT can be transported via the air for thousands of miles (*9–11*). These data are strengthened by results from radioactive fallout studies and by the recent concern over acid rain and its atmospheric link to industrial centers. There are literature data to support the contention that high amounts of toxaphene can be lost due to volatility (*12, 13*). Long-range transport of toxaphene by way of the air is well documented both by direct observation of toxaphene in air at remote sites (*14, 15*) and by inference from finding the material in organisms at sites remote from the use of this material: Great Lakes fish (*1*); Antarctic cod from the South Pacific and Arctic char from the Tyrolean Alps (*4*) and from a lake in southern Sweden (*16*).

Use of air mass trajectory analyses coupled with pollutant measurements is a relatively new procedure for confirming sources of these materials. Pack et al. (*17*) used a trajectory model to map fluorocarbon transport in Europe. Others have performed long-range mapping to follow ozone transport along the eastern coastline (*18*). Trajectory modeling was used by Rice and Olney (*19*) to confirm that toxaphene transport to Bermuda could be tied to the southeastern region of the U.S. This same type of trajectory modeling was utilized in this study in order to determine if a transport link to the cotton-growing regions (South Central to Southeast U.S.) could be established which coincided with high episodes of toxaphene occurring over Lake Michigan.

Measurements of toxaphene in air, rain, and surface water of the Great Lakes have been reported (*2*). Therefore, the potential for this route appears possible. The purpose of this study was to examine atmospheric transport of toxaphene to the Great Lakes from the high-use areas in the Southern United States. Establishing a reliable analytical method was a critical requirement to achieving this goal.

Materials and Methods

Air Collection. Toxaphene in the air was collected by passing air through an air-scrubbing system composed of a glass-fiber filter [only with the Hi-Vol (General Metals Works, Inc., Village of Cleves, OH) collectors] and a series of soft polyurethane foam plugs. Two types of collectors were used in this study. A Hi-Vol collector was used for sampling air for toxaphene where concentrations were anticipated to be low to moderate, e.g., at the Lake Michigan sampling locations on Beaver Island and at Bridgman, MI, and in St. Louis, MO. A low-volume air-sampling device was used in Greenville, MS, where levels were anticipated to be high. The high-volume sampler was a standard Hi-Vol high-volume sampling system modified by adding a stainless steel extension tube (23 cm long and 9 cm diameter) behind the filter holder (10 × 8 in.) such that two to three 9 cm diameter × 6.5 cm long polyurethane foam plugs could be installed. The air first passes through a Gelman type "A" glass-fiber filter rated at an exclusion size for aerosols in air of 1 μm. The bulk of the toxaphene is expected to be collected as a gas on the first foam plug. The second plug in the series was placed as a backup to check for possible breakthrough of toxaphene and to also preclude back flow of contamination from the pumping apparatus. The pump was a General Metal Works Model GMWL-2000 blower.

The entire sample holder was carefully cleaned prior to use by scrubbing with soap and water and solvent rinsing with pesticide-grade acetone and methylene chloride. Between each sample collection the collection assembly was additionally rinsed with pesticide-grade solvents. The filter and plugs were carefully cleaned prior to use to free them of possible contaminants. The procedure for cleaning filters involved 450 °C ignition in a muffle furnace for 4 h and storage in individual aluminum foil containers. The plugs were carefully cleaned prior to use according to the procedures of Billings and Bidleman (*20*) and periodically checked to guarantee their cleanliness prior to use.

Polyurethane foam plugs were also used for low-volume collection. These plugs measured 7 cm long × 3.5 cm diameter and were installed in glass holders (10.5 cm long × 3.5 cm diameter). No prefilters were used with these collectors, and two plugs were placed in series. These plugs were also precleaned according to Billings and Bidleman (*20*).

The flow for the Hi-Vol collection was maintained at 0.55–1.1 m^3/min, and the volumes for collection ranged from 1161 to 6727 m^3 (Table I). The flow for the low-volume collection ranged from 7 to 10 L/min. A Gast pump was used to provide the vacuum for the low-volume collector, and a Gilmont flow meter (size 3, catalog F1300) was used to monitor the flow by taking readings at 1–2-day intervals throughout the collection. A Sprague/Textron gas meter was used to measure the monthly air volumes collected. These units were calibrated at the University of Michigan Air Resources Laboratory prior to employment. To monitor the airflow of the Hi-Vol collections, a Marshalltown-type flow gauge was used at Bridgman and Beaver Island. Use of the gauges involved observation of the gauge reading 2–3 times during the 3-day sampling period and deriving an average reading for the total period of collection. With the St. Louis collection, a continuous disk chart recorder monitored the gas flow. All of the General Metal Works pumps and gauges for the Hi-Vol samples also were calibrated on the University of Michigan Air Resources Laboratory gas meter prior to use in the field.

The air collectors were operated at locations which were selected to describe a possible transport pathway for toxaphene from Greenville, MS, a region known for high use of toxaphene in the past, to Lake Michigan. Three locations, Greenville, MS, St. Louis, MO, and Bridgman, MI (Figure 1), were sampled simultaneously during four 2-week time intervals through the summer and fall of 1981. Samples were also collected from Beaver Island, in northeastern Lake Michigan, during the second and third collection period. Rain was collected from Beaver Island during the last sampling interval. The rain collectors were simple bucket collectors (total fallout collectors) which were outfitted with screen wire rings on the top edges to discourage birds from landing on them. The buckets were carefully washed with soap and water and rinsed with

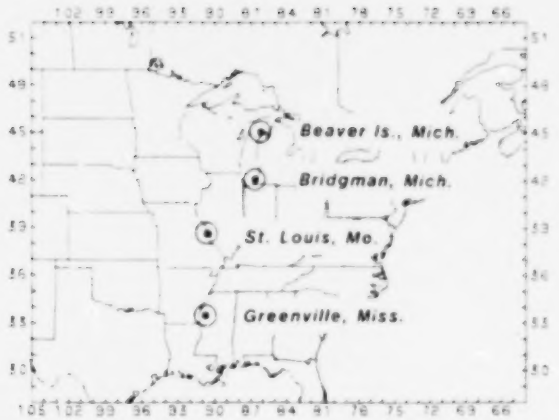

Figure 1. Locations of the four sites where air was sampled for toxaphene in the summer and fall of 1981.

pesticide-grade methylene chloride just prior to each use. For storage, the contents of the buckets were poured into precleaned brown glass 1-gallon bottoles. The interior of the buckets were rinsed with methylene chloride, and these rinses were added to the sample bottles. Additional methylene chloride (total ~200 mL/bottle) was added for stabilization in storage.

Periodic blanks were taken at each of the sampling locations. These involved all the steps of the setup for collection except for turning on the pumps. These samples were then broken down and returned to the laboratory for extraction and analysis as if they were actual samples.

Extraction. To extract the toxaphene residues from the filters and foam plugs, each was cycled with pesticide-grade petroleum ether for 12 h in a Soxhlet assembly. Following petroleum ether extraction, extracts were concentrated to approximately 5–10 mL and stored until analysis. The rain samples were extracted by mixing the sample with methylene chloride (1:3 v/v solvent to water) on a ball-mill roller for 3 h. Much thought went into how to work up the samples in a way that would maximize the identification of the toxaphene expected in the sample. Our major interests were to study any weathering which might be apparent and to avoid lengthy handling procedures which might reduce our recoveries. Nitration as a cleanup (*21*) was considered but discarded because some chemical alteration by the procedure had been reported (*5*). Silicic acid (*7*) was repeatedly tested; however, reproducibility was variable, and we felt the results could not be trusted. We finally settled on a simple treatment of the extracts with sulfuric acid, followed by direct injection and analysis by electron capture gas chromatography.

Chromatographic Analysis. Analyses of the extracts involved concentration of each sample to 1–2 mL, acid treatment with an equal volume of concentrated sulfuric acid, transfer of the organic phase, and then an initial prescreening of each sample by packed column electron capture gas chromatography. On the basis of these initial prescreenings, the volume was adjusted for final qualitative and quantitative analyses by the capillary GC. For most of these final capillary injections, a Varian 8000 autosampler was used. The injection volume was 4 μL, and the solvent was petroleum ether or hexane. The injection method was splitless with a back flush delay of 0.75 min. A toxaphene standard was usually injected for each of four samples injected. The operating conditions for the capillary instrument were as follows: the column was a (0.20 mm i.d. by 50 m long) Hewlett-Packard fused silica capillary column coated with SE-54, the carrier gas was hydrogen flowing at a linear velocity of 35 cm/min, and nitrogen was used as the makeup gas flowing at 30 mL/min. The oven temperature was programmed from 100 to 240 °C at the rate of 1 °C/min, and the other heated zones were 220 °C injector and 320 °C detector. Data handling for the capillary instrument was carried out on a Perkin-Elmer Sigma 10 data system with a basic programming upgrade. To ensure proper data slicing (discrete area slicing in small enough intervals to collect the capillary output), the Perkin-Elmer standard slicing option was overridden by forcing the instrument to operate at its maximum slicing time of 0.13 s/scan at 10-min intervals. This was determined by trial and error to give the best data treatment to the entire spectrum of each 140-min sample run. The method for processing the data was set to quantitate according to the external standard method. The retention times were calculated as relative retention time (RRT) to octachloronaphthalene which was used as the reference peak. DDE was used as a reference peak for some of the samples. These standards were added to each sample just prior to GC analyses.

To select a standard which most consistently matched the peaks that were being measured in the Greenville air samples, we examined three different toxaphene formulations used in the Greenville area (Hercules BFC 90-100, Central American 90-100, and Drexel 616 Form Chem). These were compared to our EPA Research Triangle Park standard (lot no. B610). From this study we decided that the EPA standard gave the best matches.

In order to establish an appropriate representation of toxaphene to be used for comparison with samples, standards were screened, and peaks were chosen on the basis of the following criteria. Only peaks that were well resolved and could be reproducibly identified between standard runs were considered. In order to achieve reproducibility in peak identification, i.e., relative retention time (RRT) matching, while minimizing the inclusion of close eluting peaks within the peak window, an RRT tolerance of ±0.008 was chosen. Furthermore, it was considered important that an even distribution of peaks over the total elution time for toxaphene be used. Approximately 90 peaks were selected on the basis of the above criteria. The selected peaks were then screened against expected interferences. For this study Aroclors 1242 and 1254 were especially important in the Lake Michigan and St. Louis samples, and the pesticides DDT, DDE, and chlordane were important interferences in Greenville. Those peaks which were matched to the various interfering components were removed from the peak table. During the course of our analyses, the number of peaks that met all screening criteria for standards ranged from 26 to 60. These peaks were then used to represent toxaphene for comparison with samples.

Toxaphene identification in the samples was accomplished by screening sample peaks for matches with the standard peak tables described. The criteria for peak matching in the samples were identical with those used for standard comparison. However, those peaks that were matched in the samples were further screened for possible errors in base-line treatment and for unknown interferences. Peaks occurring in the sample that were disproportionately high in area (relative to other matched peaks) were considered interfered with and were excluded from quantitation. This latter screening presupposes that the ratio of toxaphene peaks in the sample is similar to the standard. Lacking proof of this, we selectively eliminated peaks only in the most extreme case, e.g., when the (in-

Table I. Amount of Toxaphene in Air Samples from Bridgman, MI, Beaver Island, MI, St. Louis, MO, and Greenville, MS

sample location	date–time on	date–time off	air volume, m^3	toxaphene concn, ng/m^3
Bridgman, MI	07/30–1755	08/02–1605	3456	0.32
	08/02–1615	08/05–1515	3353	0.04
	08/05–1525	08/08–1550	3506	0.02
	08/08–1600	08/11–1620	3146	0.69
	08/25–1620	08/28–1230	3211	1.2
	08/28–1240	09/03–1120	6727	0.63
	09/03–1115	09/06–1635	4074	0.16
	09/28–1732	09/30–1714	3148	0.09
	10/01–1808	10/04–1210	3960	0.01
	10/09–1630	10/11–1609	2916	0.67
	10/14–1853	10/17–1645	4192	0.46
	11/05–1806	11/08–1213	4364	0.17
	11/08–1236	11/12–1236	4729	0.08
	11/14–1742	11/17–1745	3549	0.50
Beaver Is., MI	08/28–1530	08/31–1600	3924	0.05
	08/28–1530	08/31–1600	3985	0.02
	08/31–1630	09/03–1630	4709	0.23
	08/31–1630	09/03–1630	3586	0.28
	09/28–1715	10/01–1530	4131	0.02
	09/28–1715	10/01–1530	4538	0.03
	10/01–1600	10/04–1630	3871	0.03
St. Louis, MO	07/30–1530	08/02–1530	4100	0.47
	08/02–1530	08/05–1530	3577	0.56
	08/05–1530	08/08–1530	2540	4.7
	08/08–1530	08/11–1530	3058	0.51
	08/25–1200	08/28–1200	3326	5.2
	08/28–1200	08/31–1200	3192	0.86
	08/31–1200	09/03–1200	2661	0.97
	09/03–1200	09/06–1200	2925	1.2
	09/28–1530	10/01–1530	3452	1.0
	10/01–1530	10/04–1530	3542	0.40
	10/04–1530	10/07–1530	3758	0.75
	10/07–1530	10/08–1345	1161	0.51
	11/05–1530	11/08–1530	3884	0.52
	11/08–1530	11/11–1530	3456	0.37
	11/11–1530	11/12–2100	1680	1.0
Greenville, MS	07/30–1630	08/02–1630	38.23	4.3
	08/02–1630	08/05–1630	42.55	8.1
	08/05–1630	08/08–1800	43.44	11
	08/08–1800	08/11–1800	39.74	2.8
	08/25–0430	08/28–0900	39.93	7.9
	08/28–1830	08/31–1800	37.32	7.8
	09/03–0630	09/06–1800	43.09	19
	09/28–2100	10/04–2100	69.55	3.7
	10/04–2100	10/07–2100	34.78	7.4
	10/07–2100	10/10–2100	37.37	5.7
	10/10–1100	10/13–1100	10.20	22
	11/02–1000	11/05–1000	32.40	4.9
	11/05–1000	11/11–1000	64.80	3.1
	11/11–1000	11/14–1000	32.40	2.6
	11/14–1000	11/17–1000	32.40	1.8

terfered) peaks accounted for greater than 40% of the sum of the area for all of the matched peaks.

Quantitation of toxaphene in the samples was based on the ratio of the sum of the areas for peaks matched (and screened) in the sample to the sum of the areas of the corresponding peaks in the standard. This value was then multiplied by the standard concentration and sample volume to determine the total nanograms of toxaphene. The toxaphene concentration was the quotient of total nanograms of toxaphene determined to be in the sample divided by the volume of air (m^3) collected (Table I).

Quality Assurance. Blanks were found to contain no recognizable toxaphene patterns. However, some spurious peaks did match the relative retention times for toxaphene and upon quantitation averaged 23.1 ng. Therefore, the limit of detection for high-volume samples was approximately 0.06 mg/m^3, and for the low-volume samples it was 0.6 ng/cm^3. Linearity of the electron capture response to toxaphene was maintained over the standard ranges of 118–444 ppb. Sample amounts were adjusted to fall in this range.

Table II. Duplicate Results

Beaver Island sample date	toxaphene concentration, ng/m^3	relative % difference of duplicates
8/28	0.054, 0.023	43
8/31	0.23, 0.28	8
9/28	0.024, 0.031	13
		$\bar{x}$ = 21

Duplicates were run at Beaver Island. The replicate performance is shown in Table II. Averaging the results for the three duplicate sets gave a value of 21 for the average relative percent differences of these three duplicate pairs.

Modeling. Diagnostic modeling tools were applied to the measured values of toxaphene for three of the sampling sites. The diagnostic techniques used in this study take into account the potential long-range atmospheric transport of toxaphene and can include enroute processes of dry and wet deposition, chemical transformation, and dispersion. The areal probability of contribution to the toxaphene levels at a receptor is calculated in two ways. In the first, the areal probability field resulting from the ensemble of individual trajectories arriving at the receptor during the hours of sampling is calculated. This is the probability of contribution due to "natural" phenomena. It would represent the spatial distribution of contribution if emissions were universally homogeneous. In the second method, the individual trajectory probabilities are weighted proportionally to the resulting toxaphene concentrations. If there is systematic transport of the toxaphene to the receptor from a particular area or areas, the two fields will be dissimilar. On the other hand, if there is no clear "corridor" associated with the transport of toxaphene, then there will be little difference between the weighted and unweighted contribution probability fields.

The transport of the air to monitoring locations was estimated by using the NOAA ARL-ATAD trajectory model (22). This model estimates the upwind track of the wind for the "mixed layer" of the atmosphere (a layer from the surface to roughly 1500 m above the surface in the summer and 800 m above the surface in the winter). The determination of the potential for upwind areas to contribute to toxaphene concentrations at a receptor can be expressed as a two-dimensional probability field (23). It was assumed that each trajectory represented the center-of-mass of probability for air to be transported to a receptor. The transport potential for a given sampling time included the mean transport computed by using the trajectory model plus the uncertainty imposed by the atmospheric dispersion which occurred en route. The probability of a reactive, depositing tracer arriving at a point $\mathbf{x}$ at a time t, $A_r(\mathbf{x},t)$, can be expressed as (cf. ref 24 and 25)

$$A_r(\mathbf{x},t) = \int_{t-\tau}^{t}\int_{-\infty}^{\infty}\int_{-\infty}^{\infty} Q(\mathbf{x},t|\mathbf{x}',t')R(t|t')D_r(\mathbf{x}',t')\Lambda_r(\mathbf{x}',t')\,d\mathbf{x}'\,dt' \quad (1)$$

where $Q(\mathbf{x},t|\mathbf{x}',t')$ is the probability of an air parcel located at $\mathbf{x}'$ at time t' arriving at a receptor $\mathbf{x}$ at time t, $R(t|t')$ is the probability of the tracer not being reacted to another species from t' to time t, $D_r(\mathbf{x}',t')$ is the probability that the tracer will not be dry deposited at $(\mathbf{x}',t')$, and $\Lambda_r(\mathbf{x}',t')$ is the probability that the tracer will not be wet deposited at $(\mathbf{x}',t')$. The integration was continued over a period τ which was prescribed in this study as 72 h (or less if the trajectory calculation terminated prematurely due to

missing input data). The last three probability functions on the right side of the equation are not well-defined for toxaphene. As a starting part it was assumed that toxaphene was *not* reactive or depositing. This assumption has no impact upon the results of this study because we are studying the relative difference in potential between two fields computed using the same assumptions. Differential distributions of precipitation could have an impact upon even the relative difference in probability, but quantitative estimates of precipitation rates for 1981 were not available when this modeling exercise was conducted.

The potential mass transfer function, $Q(\mathbf{x},t|\mathbf{x}',t')$, is also poorly understood but can be approximated as a first guess from the computation of upwind trajectories. The axis of the computed trajectory was assumed to represent the highest probability at any time upwind for contributing to the toxaphene composition at the monitor. The spatial distribution of the potential mass-transfer function away from the axis of the trajectory will depend upon the degree of vertical mixing, coupled with the magnitude of the wind velocity shear. As a first approximation, it was assumed that the puff of potential mass transfer was normally distributed above the trajectory with a standard deviation which increased linearly with time upwind (*23*, *26*, *27*). Thus, $Q(\mathbf{x},t|\mathbf{x}',t')$ is assumed to be expressed as

$$Q(\mathbf{x},t|\mathbf{x}',t') = \frac{1}{2\pi\sigma_x(t')\sigma_y(t')} \exp\left[-\frac{1}{2}\left(\left(\frac{x''(t')}{\sigma_x(t')}\right)^2 + \left(\frac{y''(t')}{\sigma_y(t')}\right)^2\right]\right. \quad (2)$$

where $x'' = X - x'(t)$ and $y'' = Y - y'(t')$ with (X, Y) being the coordinates of the grid and $x'(t')$ being the coordinates of the centerline of the trajectory. It is assumed that σ_x and σ_y can be approximated by

$$\sigma_x(t') = \sigma_y(t') = at' \quad (3)$$

with a dispersion speed, a, equal to 5.4 km h^{-1} (*26*).

The integrated potential mass transfer for a given trajectory, j, arriving at time t can be calculated as

$$\bar{Q}_j(\mathbf{x}|\mathbf{x}') = \frac{\int_{t-\tau}^{t} Q(\mathbf{x},t|\mathbf{x}',t')\,dt'}{\int_{t-\tau}^{t} dt'} \quad (4)$$

The ensemble of integrated potential mass-transfer functions, calculated for each trajectory, were averaged over the toxaphene sampling periods to obtain estimates of the mean potential mass transfer for each sample. It was this time-averaged potential mass transfer which is used for comparison in this study.

The measured concentrations of trace elements were then used to derive an "implied" transport bias. Potential mass-transfer fields calculated for each trajectory, j, were weighted by the toxaphene concentrations measured at that time, resulting in a concentration-weighted mass-transfer potential field, $\bar{Q}(\mathbf{x}|\mathbf{x}')$, calculated as

$$\bar{Q}(\mathbf{x}|\mathbf{x}') = \left[\frac{\sum_{j=1}^{J} \bar{Q}_j(\mathbf{x}|\mathbf{x}')\ \chi_j(\mathbf{x})}{\sum_{j=1}^{J} \chi_j(\mathbf{x})}\right] \quad (5)$$

where $\chi_j(\mathbf{x})$ values are the concentrations of the toxaphene associated with each trajectory, j. The percent difference between the weighted and unweighted fields represents the magnitude of variation from the assumption that sources of toxaphene are spatially homogeneous. While these assumptions limit the interpretation of results, the comparison of weighted vs. unweighted contribution fields still provides a useful first test of the hypothesis that the toxaphene is being transported to the receptors from source fields in the Southern United States.

Results and Discussion

Analytical Results. The concentrations of toxaphene measured in the air collected at the four sampling sites are listed in Table I. The levels were highest in Greenville, MS (average of 7.0 ng/m^3), followed by St. Louis, Mo (1.3 ng/m^3), and lowest in Bridgman (0.35 ng/cm^3) and Beaver Island, MI (0.10 ng/cm^3). The chromatographic peaks that were matched averaged 37% (of 36 peaks) for Lake Michigan (Bridgman plus Beaver Island), 39% (of 39 peaks) for St. Louis, and 51% (of 55 peaks) for Greenville. These values provide an estimate of the similarity of the material measured to the standard. One interpretation of this might be that the toxaphene in Greenville is a better match since it is closer to the source than the material measured in air at St. Louis or near Lake Michigan. And correspondingly that increasing distance from the source causes changes in the composition (lower percent match) of the toxaphene mixture (often expressed as "weathering"). Another interpretation might be that the lower match percents are merely a function of the smaller amount of material in the samples at the more northern sites. Regression analyses on the amount of toxaphene measured vs. the percentage of peak matched with each sample subset (Greenville, Bridgman, St. Louis, and Beaver Island), however, were not found to be significant. Therefore, the degree of alteration of the toxaphene mixture does, in fact, appear to be related to the distance from the likeliest source regions which we propose are in the Southern United States.

Table I also lists the total volume of air collected for each sample. Regression analyses of this parameter vs. the concentrations measured were carried out for each sample subset. No significant correlations were found for any of the high-volume collections taken in the northern sampling sites. However, a positive correlation was found for the Greenville site, i.e., the greater the air volume sampled, the lower the total nanogram amount. This finding led to further tests to see if breakthrough of the toxaphene could be observed on the low-volume backup plugs. Recall that the Greenville sampling plugs were smaller than the Hi-Vol plugs. No toxaphene, however, was found on the backup plugs; therefore, breakthrough did not appear to be occurring. This was consistent with extensive tests previously performed by us to determine the efficiency of polyurethane foam for trapping of toxaphene vapors (*28*). Since breakthrough was not occurring with the low-volume collectors, there appears to be no obvious explanation for the lower values found when higher volumes of air were sampled in Greenville.

Filter retention of toxaphene was less than 5% of the total measured toxaphene for the Hi-Vol collections, and nothing was found on the backup plug. Therefore, only the first plug analyses were used in reporting the toxaphene amounts presented here.

Figures 2 and 3 present the results listed in Table I in graphic form. It is apparent that for each of the locations an increase occurred in amount of toxaphene from the first sample period in early August to early September, whereupon a gradual decline in concentration was observed for the October and November sampling periods. Table III presents these findings in average concentrations (weighted according to the duration of the sampling pe-

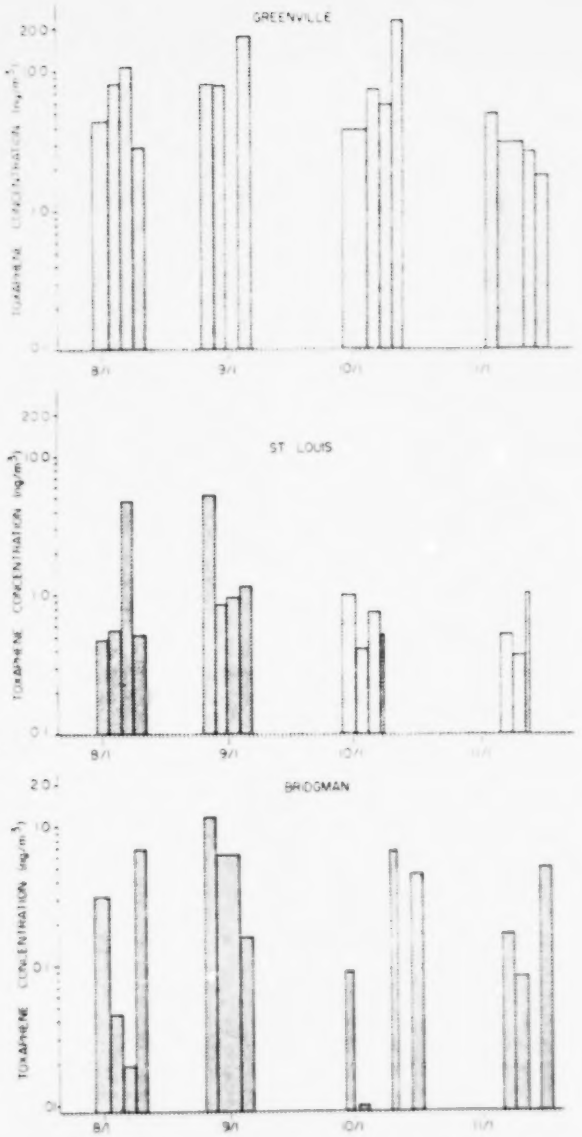

Figure 2. Simultaneous determinations of toxaphene in air measured at four sites lying along a general south-to-north transect from Greenville, MS, through St. Louis, MO, and ending in the Lake Michigan area (Bridgman and Beaver Island, MI). The vertical axes are in log units, and the horizontal axes are calendar dates.

Table III. Trend in Toxaphene Concentration at Sampling Sites for the Summer and Fall of 1981

	average toxaphene concentration by location, ng/m³			
sampling interval	Beaver Island, MI	Bridgman, MI	St. Louis, MO	Greenville, MS
August		0.27	1.6	6.5
September	0.14	0.79	2.1	11
October	0.03	0.30	0.70	8.6
November		0.23	0.54	3.1

riod) for each of these discrete sampling periods.

This trend for toxaphene levels in air observed in our data was similar to the trend for relative levels of atmospheric toxaphene observed by Arthur et al. (*29*) in the Mississippi Delta in 1972–1974. In the Arthur et al. study, the maximum average toxaphene occurred in August/

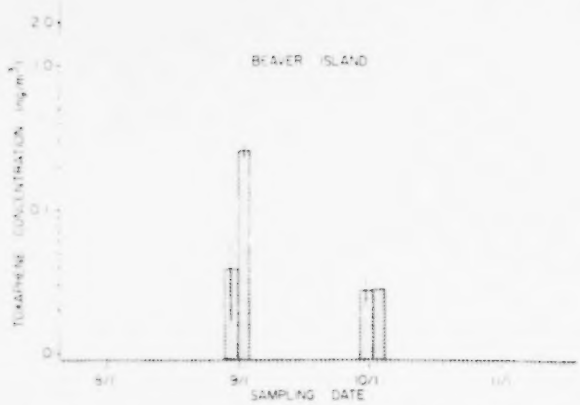

Figure 3. Toxaphene in air measured at Beaver Island, MI, from August 28 to October 4, 1981. Vertical axis is in log units, and the horizontal axis is in calendar dates.

September periods: 1540 ng/m³, Aug 1972; 269 ng/m³, Sept 1973; 903 ng/m³, Aug 1974. These average concentrations were considerably higher than measured by us. However, toxaphene usage was much less in 1981 than in the early 1970s (*2*).

In looking at Figure 2, one might expect some similarities in concentration patterns between the three locations, especially if an atmospheric link is predicted. For example, the first interval bears a close resemblance in general pattern between St. Louis and Greenville. There appears to be a tendency to observe possible shifts by one sampling period of the high level of toxaphene observed at one location to an appearance of this material as a high level in a more northerly location a few days later (notice such a connection for St. Louis to Bridgman for the first sampling period, Figure 2). Keep in mind that the scale for the Bridgman figure is a factor of 10 less than the two other sites depicted.

One rain sample was collected from Beaver Island, MI, while air measurements were being made from September 28, to October 2, 1981. The sample contained 31.6 ng/L of toxaphene with 38% of the possible peaks matched.

Modeling Results. One goal of this study was to use the previously presented data as a basis for proposing some boundary limits for toxaphene transport to Lake Michigan. We chose an atmospheric transport model to assist in these estimates.

The probability fields predicted by using this approach are referred to as natural potential fields. They quantify the possibility of contribution from any upwind area to a particular receptor without regard to the actual placement of emission sources.

The "natural potential" for contribution to toxaphene concentrations at the Bridgman, MI, site is shown in Figure 4. This figure shows the natural potential for contribution in units of 10^{-6} km^{-2}. The plot shows that the highest occurrence of winds during the sampling periods was from the southwest of the receptor. The implied transport field (not shown) was not substantially varied from the spatial pattern found for the unweighted case in Figure 4. The dissimilarity of the two fields was discerned only by calculating the percent difference between the weighted and unweighted fields as shown in Figure 5. This plot suggests that there was a slight spatial bias for above-average toxaphene concentrations to be associated with winds from the south to southeast, but the magnitude of the difference in the weighted and unweighted fields is small, representing a signal of only 10% bias from that field expected

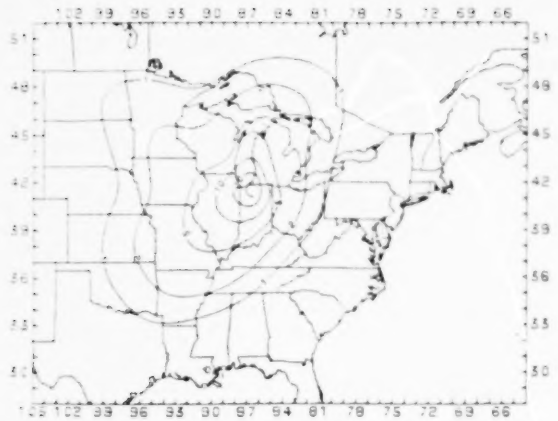

Figure 4. Unweighted probability of contribution during the sampling periods in units of 10^{-6}/km^2 in Bridgman, MI (approximate center of concentric rings).

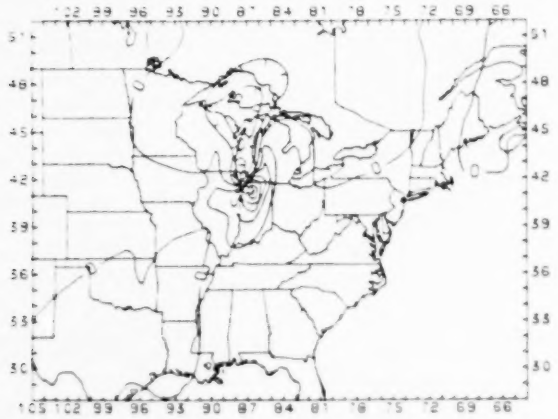

Figure 5. Difference between unweighted probability of contribution and weighted probability of contribution during the sampling periods in units of 10^{-6}/km^2 in Bridgman, MI (approximate center of concentric rings). The hatched lines within the probability contours indicate negative values.

if emissions were spatially homogeneous.

Figure 6 shows the percent difference of unweighted and weighted fields, respectively, for the receptor at St. Louis, MO. These results are based on the 15 samples collected there in 1981. The probability field in Figure 6 has a markedly higher amplitude than was apparent at the Bridgman, MI, site (Figure 5). Here the analyses suggest a more well-defined bias in transport of above-average concentrations from the south, supportive of the hypothesis that the toxaphene was being transported from regions of application in the Southern United States.

The difference of the unweighted probability field and the weighted fields for Greenville, MS, is plotted in Figure 7. These results indicate that a relatively large bias is exhibited by the data and that the preferred transport paths for above-average concentrations of toxaphene at the Greenville site were strongly associated with winds originating along the Gulf Coast. Winds from the north are systematically associated with lower than average concentrations.

The analysis of transport corridors for Beaver Island, MI, samples was not conducted because only four samples were available for that site.

It has been assumed that each trajectory during the sample period was equally responsible for the observed concentration. However, without better temporal resolu-

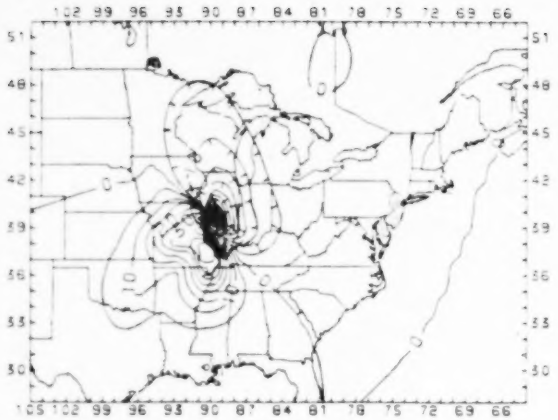

Figure 6. Difference between unweighted probability of contribution and weighted probability of contribution during the sampling periods in units of 10^{-6}/km^2 in St. Louis, MO (approximate center of concentric rings). The hatched lines within the probability contours indicate negative values.

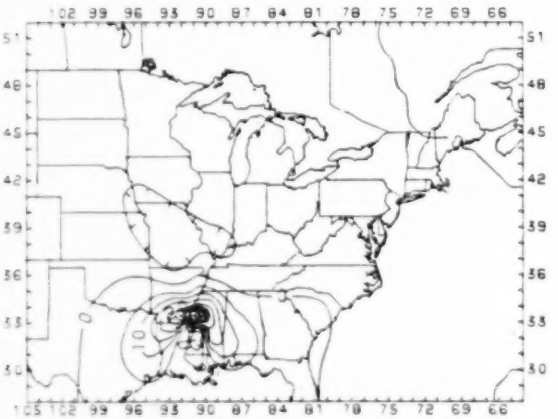

Figure 7. Difference between unweighted probability of contribution and weighted probability of contribution during the sampling periods in units of 10^{-6}/km^2 in Greenville, MS (approximate center of concentric rings.) The hatched lines within the probability contours indicate negative values.

tion in the sampling, it is difficult to assess the uncertainty inherent in this assumption. For comparison, the transport of atmospheric trace elements is highly episodic. The dry deposition of trace elements, assuming the process is proportional to the ambient concentration, is highest during specific episodes of roughly 3 or 4 days of duration (*30*, *31*). The significance of such episodic contribution could be lost in this analysis if the episode were split by two or more long-period samples. The diagnostic methodology developed for this study is designed to be employed with a larger data base. The sample size available in this study limits the use of ensemble analyses.

Nonetheless, the results of this diagnostic analysis of the measured toxaphene concentrations shows a consistent pattern. At all measurement locations the toxaphene corridor was associated with southerly winds. The preferred corridors of transport of higher concentrations increased from northern to southern measurement sites, presumably in response to the larger range of concentrations in the south. While this analysis is not capable of proving which source region(s) contributed to the observed concentrations, the results do suggest that higher than average atmospheric toxaphene concentrations were associated with advection from the south.

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Registry No. Toxaphene, 8001-35-2.

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